

STUDY IN COMETARY

ASTROPHYSICS

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ABSTRACT

The investigation of the vacuum ultraviolet photolysis of acetylene has been completed and a paper has been prepared for publication. This is being submitted for approval under separate cover.

Studies under current investigation include:

- a) the reaction of OH radicals with CH_4 at 25°C and at -195°C .
- b) the reaction of NH and NH_2 radicals with CH_4 at 25°C and at -195°C .
- c) the electron bombardment of water at -195°C with 5KEV electrons.

In addition, equipment is being assembled for:

- a) proton bombardment of low temperature solids and
- b) vacuum ultraviolet flash photolysis of low temperature solids using a Garton flash lamp.

1. ENERGY DISSIPATION FROM ELECTRONICALLY EXCITED ACETYLENE

1.1 Introduction

There has been wide speculation on the gaseous composition of comets. Spectral information directly related to this problem has been obtained from the large number of free radicals that emit light in the visible by a fluorescence mechanism. Direct information on the nature of the parent compounds is not available but can be obtained in the laboratory by vacuum ultraviolet photolysis at very low pressures. These experiments are expected to find molecules that will produce the free radicals of interest by a simple photodissociation of the molecule.

The work accomplished on the photochemistry of acetylene has been discussed in previous reports, namely: the observation of C_2 swan system in emission, the effect of wavelength and pressure on the intensity of the emission and the formation of molecular hydrogen. The investigation has been completed this quarter with an examination of the effect of pressure on quantum yield for hydrogen formation and quantum yield for acetylene disappearance. This has led to some new results regarding the fate of the electronically excited acetylene molecule formed upon absorption of light at 1236\AA .

1.2 Results

The effect of pressure of acetylene on the molecular hydrogen formed and on the amount of acetylene reacted in photolysis at 1236\AA is shown in Table 1. The following points should be noted:

(1) The quantum yield for hydrogen formation is considerably larger in the micron pressure region than in the pressure range of a few mm Hg. This parallels the effect of pressure on intensity of C_2 emission previously reported.

(2) The quantum yield for the disappearance of acetylene is small in the micron region but is of the order of unity in the mm Hg region. This parallels effect of pressure on polymer formation.

(3) Hydrogen formation accounts for 1/2 to 1/3 of the acetylene reacted at low pressures, but is a very minor (2%) process at higher pressures.

(4) At low pressure, major portion of energy absorbed does not result in chemical conversion of acetylene.

(5) The hydrogen pressure vs. time plots are linear for the 56 μ experiments, increasingly curved at 112 μ and 180 μ and very badly curved at 2.4 mm Hg.

(6) Only small changes were noted in absorbed intensity after photolysis of acetylene in micron region, but a decrease by a factor of 40 was evident after the completion of the 2.4 mm Hg experiment which correlated with observable polymer deposit on the LiF entrance window.

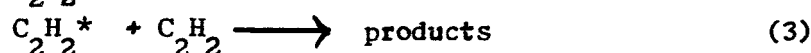
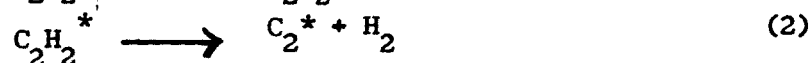
TABLE 1

Hydrogen Formation and Acetylene
Disappearance in Photolysis of Acetylene at 1236 \AA

Pressure of C_2D_2 (u Hg)	56	112	180	2400
I_a (quanta/sec) $\times 10^{14}$	8.10	15.4	22.9	39.0
R_{D_2} (molec/sec) $\times 10^{14}$	0.79	2.01	1.90	0.82
$R_{\text{C}_2\text{D}_2}$ (molec/sec) $\times 10^{14}$	1.59	4.83	8.09	~ 35
D_2 (molec/quanta)	0.10	0.13	0.08	0.02
C_2D_2 (molec/quanta)	0.20	0.31	0.35	~ 1
$\text{C}_2\text{D}_2/\text{D}_2$	2.0	2.4	4.2	50

1.3 Discussion

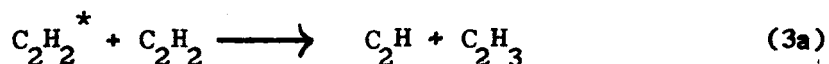
The fact that both C_2 emission and molecular hydrogen formation are reduced with increasing pressure suggests that both arise from decomposition of the electronically excited acetylene molecule formed in the primary photochemical act and that the excited molecule suffers quenching by collision with acetylene molecules



The fact that at lowest pressure used, the quantum yield for the disappearance of acetylene is only 0.2, indicates that 80% of the electronically excited molecules lose energy, probably by collision with the wall of the reaction vessel, without emitting light or decomposing.



The increased importance of polymer formation at high pressure of acetylene is one measure of the occurrence of reaction 3. Since, even at the lowest pressure, molecular hydrogen accounts for only one-half of the acetylene decomposed, the occurrence of reaction 3 giving polymer and/or ethynyl and vinyl radicals,



is estimated to be of comparable importance to 2. The formation of an electronically excited acetylene molecule at 1236\AA capable of suffering collision before decomposing is consistent with the vibrational structure observed in the absorption spectrum of acetylene in this region.¹

The fate of this excited molecule is controlled by conditions of the laboratory experiment in that deactivation occurs by collision with other acetylene molecules and by collision with the wall of the reaction vessel. At very low pressure and with an infinite "reaction vessel", the decomposition of electronically excited acetylene resulting in C_2 emission should tend to occur with nearly unit quantum efficiency. These conditions could be realized in the coma of a comet.

2. REACTIONS OF OH AND NH_2 RADICALS WITH METHANE

2.1 Introduction

These studies have been initiated to develop an understanding of free radical reactions that could occur in the nucleus of a comet, or in the gas phase immediate to the surface of the nucleus. The present series of experiments will investigate all the radicals and reactions that can be produced from mixtures of CH_4 , H_2O and NH_3 from $25^\circ C$ to $-195^\circ C$.

It is possible to produce the OH and NH_2 radical from water² and ammonia³ respectively and to study their reaction with CH_4 by photolyzing mixtures with $\lambda > 1450\text{\AA}$. In these experiments a hydrogen discharge lamp was used with sapphire windows.

2.2 Results

Some preliminary experiments were performed on photolysis of pure water vapor and on photolysis of pure ammonia. The reaction cell, which had provision for circulation, was fitted with a sapphire window and had a volume of 295 cc. Hydrogen was the only non-condensable product formed in each case and the rate of production of hydrogen was linear with time up to 15 minutes for water and to at least 25 minutes for ammonia. Lamp intensities were estimated by measuring the rate of

CO formation in photolysis of CO_2 for which a quantum yield of unity has been determined.⁴ Quantum yields based on this actinometry are:

0.40 ± 0.02 for hydrogen from water vapor and

0.46 ± 0.02 for hydrogen from ammonia.

In the gas phase photolysis of mixtures of a) water and methane and b) ammonia and methane the only product detected was ethane. At this time, analysis for hydrogen and products in very low concentration was not attempted. The effect of photolysis time and methane pressure on the pressure of ethane formed subsequent to photolysis of 20 mm of water vapor is shown in Table 2.

TABLE 2

Ethane Formation in Photolysis of H_2O in Presence of CH_4

Photolysis time (min)	CH_4 pressure (mm Hg)	C_2H_6 pressure (μ Hg)
15	30	53
30	30	100
60	30	120
30	5	30
30	30	100
30	50	128

The effect of the same parameters on the pressure of ethane formed subsequent to photolysis of 20 mm of ammonia is shown in Table 3.

Photolysis of water-methane and of ammonia-methane deposits (30 minutes) at -196°C with the hydrogen discharge lamp (1650\AA) did not result in formation of ethane in either case. In addition, although hydrogen is readily detected as a product of gas phase photolysis for both water and ammonia, photolysis of solid water and solid ammonia

(3 hours) at -196°C with the hydrogen discharge lamp did not result in the formation of detectable amounts of hydrogen.

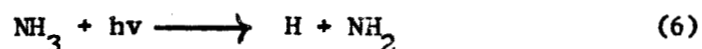
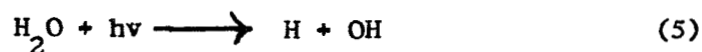
TABLE 3

Ethane Formation in Photolysis of Ammonia in Presence of Methane

Photolysis time (min)	CH_4 pressure (mm Hg)	C_2H_6 pressure (μ Hg)
15	20	17
30	20	21
60	20	27.5
30	5	6
30	20	21
30	40	32.5

2.3 Discussion

The observation that the quantum yield for hydrogen from photolysis of water and from the photolysis of ammonia approaches one-half suggests that the primary processes 5 and 6, which have unit quantum efficiency,



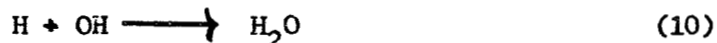
are followed mainly by hydrogen atom recombination on the walls



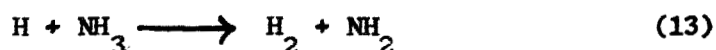
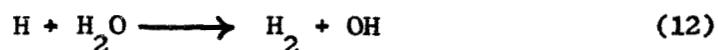
and by radical-radical recombination forming hydrogen peroxide from OH radicals and hydrazine from NH_2 radicals,



Significant contribution from back reactions

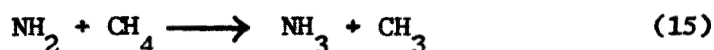
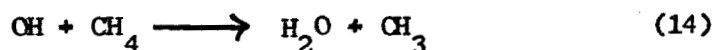


would reduce the quantum yield for hydrogen formation and occurrence of

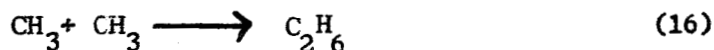


would be reflected in quantum yields larger than 0.5 for hydrogen production.

Thus, in the presence of an excess of methane, OH and NH_2 should react according to



with some possible contribution from radical-radical combination forming peroxide or hydrazine. The observation of ethane as a product of the photolysis of water or ammonia in the presence of methane may be taken as evidence for the occurrence of 14 and 15, followed by methyl radical combination



The increase in rate of production of ethane with increase in methane pressure for both the water and ammonia systems (Tables 2 and 3) is in qualitative agreement with occurrence of 14 and 15. The considerably lower rate of production of ethane found in the ammonia-methane system suggests that either or both of the following are occurring:

a. NH_2 radicals abstract hydrogen from methane at a rate about one-fifth that for abstraction by OH radicals.

b. NH_2 recombination to form hydrazine occurs to a much greater extent than recombination of OH to form hydrogen peroxide.

The fact that ethane is not produced from the same systems in the solid phase at -196°C means that methyl radicals are probably not being produced at this wavelength and that reaction 14 and 15 are not occurring in the solid. This could be because OH and NH_2 do not abstract from methane at this temperature or because OH and NH_2 are not produced by photolysis of the solids at 1650\AA .

3. ELECTRON BOMBARDMENT OF LOW TEMPERATURE SOLIDS

3.1 Introduction

To evaluate the role of cosmic radiation, i.e., chemical reactions, production of active species, etc., in cometary phenomena, the effect of charged particles (electrons or protons) on low temperature solids (H_2O , CH_4 , NH_3 , etc.) is of interest. Our initial effort concerns bombardment of water at -196°C with 5KEV electrons. Equipment is being assembled for proton bombardment experiments.

3.2 The Electron Source

The electron source⁶ was the gun element from a cathode ray tube (type 5CP1A) which was sealed into the side of a liquid nitrogen dewar. This electron source together with an oscilloscope (Dumont 304-H) provided up to 10^{-7} amperes of electron beam current. The position and size of the beam could be adjusted by the oscilloscope controls. The cathode of the tube was operated at -1400 volts with respect to ground, with the electron being further accelerated to a total of 5,000 volts before striking the ice deposited on a copper block maintained at -196°C .

3.3 Results and Discussion

At an electron current level of 10^{-8} amps, the ice deposit exhibited a blue luminescence which could be visually observed in a darkened room. With ostensibly no deposit on the copper block at -196°C ,

a considerably weaker emission was discernable which could be due to minute traces of water from various parts of the system depositing on the cold copper block. Initial spectra have been obtained using a Hilger E517 Raman Spectrograph with glass optics and recorded on type 103a0 plates. Due to the low level of the intensity of the emission, these initial spectra were obtained with relatively large entrance slits (1 mm). The spectra thus recorded show a continuum extending from 3000\AA to 5000\AA . In the absence of definitive spectra, the qualitative observation may be made that both the electron induced emission reported here and the photon induced emission previously reported from ice deposited at -196°C may be visually characterized as blue. Discussion regarding any similarities between the two results or regarding the nature of the emitting specie (whether it be the same in each case or not) must await further investigation of the phenomena and the recording of more refined spectra.

4. FUTURE WORK

Quantum yields for ethane formation will be determined in photolysis of water in the presence of methane and of ammonia in the presence of methane. If the efficiency of the primary act is unity and if each OH or NH_2 is replaced by CH_3 (reaction 14 and 15), the quantum yield for ethane formation should be one-half. In addition, use of deuterated compounds ($\text{D}_2\text{O} + \text{CH}_4$, $\text{ND}_3 + \text{CH}_4$, $\text{H}_2\text{O} + \text{CD}_4$, $\text{NH}_3 + \text{CD}_4$) should enable conclusions to be made on the reaction mechanism. The solid phase photolysis will be attempted with both the Xe resonance line (1470\AA) and the Kr resonance line (1236\AA) to compensate for shift of absorption of solid to shorter wavelengths.⁵

The electron bombardment of low temperature solids will continue in the next quarter. Further spectral measurements and kinetic studies of the decay will be made. The chemical system $\text{CH}_4 + 6\text{H}_2\text{O}$ at -195°C will be investigated for chemical reactions and emissions.

It is expected that construction and assembly of components for the proton source and the Garton vacuum ultraviolet flash lamp will be completed during the next quarter and preliminary work will be started on low temperature solids.

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